SPECIAL REPORT 95-26

Enhanced Preservation of Volatile Organic Compounds in Soil With Sodium Bisulfate

Alan D. Hewitt

November 1995

Abstract

Sodium bisulfate ($NaHSO_4$) was evaluated as a means of chemically preserving soil samples to prevent the microbiological degradation of volatile organic compounds (VOCs). Laboratory sample treatment consisted of spiking soil samples held in glass ampoules with aqueous solutions containing eight different VOCs or gasoline and then sealing them to eliminate volatilization as a concern. Samples preserved with $NaHSO_4$ were held at room temperature (22°C), while equal numbers of unpreserved samples were stored refrigerated (4°C) and at room temperature. Results show that concentrations of all of the halogenated hydrocarbons tested (14) remain fairly constant, independent of temperature or preservation. In contrast, all the aromatic hydrocarbons (10) tested as separate analytes, or ones that could easily be identified in gasoline, experienced a complete (>95%) loss when held for nine days at room temperature. Refrigeration reduced the rate of biodegradation, but two aromatic hydrocarbons showed substantial losses (>80%) within the currently recommended 14-day holding period. Over a 28-day refrigerated period, reductions of greater than 95% occurred for 9 of 10 aromatic hydrocarbons tested. With the exception of styrene, chemical preservation by introducing $NaHSO_4$ mitigated the loss of all of aromatic hydrocarbons tested over a 28-day holding period when samples were stored at room temperature. Therefore, $NaHSO_4$ preservation is one way of effectively eliminating biodegradation of VOCs in soil samples intended for low level (<1-µg/g) analysis.

For conversion of SI units to non-SI units of measurement consult ASTM Standard E380-93, *Standard Practice for Use of the International System of Units,* published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

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US Army Corps
of Engineers
Cold Regions Research &
Engineering Laboratory

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Alan D. Hewitt

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PREFACE

This report was prepared by Alan D. Hewitt, Research Physical Scientist, Geological Sciences Division, Research and Engineering Directorate, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.

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INTRODUCTION

Most soil samples collected during site investigations for establishing the presence and concentration of volatile compounds (VOCs) are sent to off-site laboratories for analysis. To allow for some flexibility between sampling and analysis operations, the U.S. Environmental Protection Agency (U.S. EPA 1986) has recommended that samples be stored at 4°C, and held no more than 14 days. This practice continues although it is well-recognized that soils can remain biologically active under these conditions. While several efforts have been made to demonstrate the magnitude of this potential problem (Jackson et al. 1991, Maskarinec et al. 1992 King 1993), only recently have studies been designed to eliminate confounding of biodegradation and volatilization losses (Hewitt 1994, Hewitt 1995a,b, Turriff 1995). These efforts are the first to assess only the biological influence on VOCs in soil samples held at 4°C.

Our approach has been to seal treated samples in glass ampoules before exposing them to various holding and storage conditions (Hewitt 1994, Hewitt 1995 a,b). Here we assess the concentration stability of 24 (see Table 1) of the 56 analytes currently identified by the Environmental Protection Agency as hazardous VOCs (U.S. EPA 1986, SW-846, Methods 8240/8260), and gasoline. Experiments look at both the effect of chemical preservation and temperature on analyte concentration in soil samples held over a 28-day storage period under conditions that eliminated volatilization losses. The preservative chosen was sodium bisulfate ($NaHSO_4$). A sufficient quantity of this salt was used so that pH 2 or less was obtained, once the soil sample was made into an aqueous slurry. The selection of this chemical preservative was based on its low toxicity, compatibility with field operations, and its success in a study of VOC stability in aqueous matrices (Maskarinec 1990). The 28-day storage period was selected based on the success of an earlier study (Hewitt 1995) and efforts to establish longer proven holding times for VOCs in preserved aqueous matrices.*

Here, spiked soil samples were stored in sealed glass ampoules, and analyzed after transfer to volatile organic analysis (VOA) vials containing water. Once VOA vials were capped, the ampoules were broken, dispersing the contents in preparation for static headspace gas chromatography (HS/GC) analysis. Using this protocol, we never exposed the spiked soils to the atmosphere, allowing biodegradation and chemical preservation studies to be performed independent of volatilization. This experimental procedure is consistent with practice of retaining soil samples in either vaportight glass bottles while they await laboratory subsampling and analysis (this practice is not recommended by the author [Hewitt et al. 1995]), or in VOA vials for low level purge and trap gas chromatography mass spectrometry (PT/GC/MS) analysis as recommended in Method 5035, a method scheduled for inclusion in the proposed third update of the SW-846, U.S. EPA (1986).

EXPERIMENTAL SECTION

The silty-sand topsoil used in this study was obtained locally from between 5 and 10 cm below the ground surface just before the start of this

* Personal communication with David Bottrell, U.S. Department of Energy, Washington, D.C., 1995.

Table 1. Volatile organic compounds and petroleum products studied during holding time and chemical preservation experiments.

	Abbrev.*	Solubility (mg/L)	o/w† Log P	Vol.†† (µL)	CAS
Set 1					
Benzene	Ben	1780	2.13	5.7	71-43-2
Toluene	Tol	515	2.65	5.8	108-88-3
Ethylbenzene	E-Ben	152	3.13	5.8	100-41-4
p-Xylene	p-Xyl	200	3.18	5.8	106-42-34
o-Xylene	o-Xyl	152	2.95	5.7	95-47-6
trans-1,2-Dichloroethene	TDCE	600	2.09	3.5	156-60-5
Trichloroethene	TCE	1100	2.53	3.7	79-01-6
Tetrachloroethene	PCE	150	2.60	3.1	127-18-4
Set 2					
m-Xylene	m-Xyl	173	3.20	5.8	108-38-3
Methylene chloride	MC	20,000	1.30	3.8	75-09-2
1,1-Dichloroethane	1,1 DCA	5500	1.78	4.1	75-34-3
Chloroform	CF	8000	1.97	3.4	67-66-3
1,2-Dichloroethane	1,2 DCA	8690	1.48	4.0	107-06-2
Bromodichloromethane	BDCM	4500	1.88	2.5	75-27-4
1,1,2-Trichloroethane	1,1,2 TCA	4500	2.18	3.5	79-00-5
Chlorobenzene	CB	500	2.84	4.5	108-90-7
Set 3:					
Styrene	Styrene	300	2.95	5.5	100-42-5
Isopropylbenzene	iso-PB	50	3.66	5.8	98-82-8
n-Propybenzene	n-PB	55	3.57	5.8	103-65-1
n-Butyl benzene	n-BB	11.8	4.29	5.7	104-51-8
Carbon tetrachloride	C-tet	800	2.83	3.1	56-23-5
1,3-Dichlorobenzene	1,3 DCB	69	3.38	3.9	541-73-1
cis-1,2-Dichloroethene	CDCE	?	?	3.9	?
1,2-Dichloropropane	1,2 DCP	2700	2.28	4.3	78-87-5
Set 4:					
Gasoline	Gas			95	

* Abbreviation.
† Octanol–water partition coefficient.
†† Volume.

experiment. It was air–dried for 24 hours, reducing the moisture content (weight percent relative to dried soil) from 24 to 4.3% (ASTM D2216-66) passed through a 30-mesh sieve, and thoroughly mixed. The organic carbon content was 0.94±0.04% (Hach method 8097). Subsamples of 1.00±0.01 g were transferred to 2-mL glass ampoules (Wheaton, actual vol. ≈ 3.1 mL) some of which already contained 0.25 g of $NaHSO_4$ as a chemical preservative (Table 2). Sodium bisulfate has a pKa of 1.92, and the quantity used created a pH of about 1.9, once sufficient water was added to produce a slurry condition. For the series of experiments described here, 15 ampoules contained both $NaHSO_4$ and moist soil, and 27 contained just moist soil.

The fortification solution was prepared by separately adding microliter volumes (Table 1) of eight neat (reagent grade) VOCs or unleaded gasoline to a 100-mL volumetric flask containing about 102 mL of groundwater. The quantities of the neat analytes added would have created an aqueous concentration of approximately 50 mg/L, if dissolution were complete. However, this is unlikely based on their solubilities. After adding either eight analytes or gasoline, the solution was manually shaken; then a Teflon stirring bar was introduced and the flask topped off with water, leaving less than 0.5 mL of headspace. These solutions were stirred for at least 24 hours and then allowed to sit undisturbed for 1 hour prior to removing aliquots.

Each soil sample was spiked with a 200-µL aliquot from the prepared aqueous solution by using a 500-µL glass syringe (Hamilton). To avoid undissolved low density analytes that would ac-

cumulate at the surface, aliquots were taken well below the water/air interface, and the stainless steel needle was wiped prior to inserting into the ampoule's neck. Before transferring a spike, each ampoule was placed in a metal tension clamp so it could be heat-sealed with a propane torch immediately after spiking. Once sealed, every ampoule contained 1 g of soil and the moisture content had been returned to 24%. In addition to preparing the soil samples, a 200-µL aliquot of the spiking solution was placed into each of three auto sampler headspace vials (22 mL, Tekmar) containing 15 mL of type 1 water. Each vial was immediately capped with a crimp-top cap and Teflon-faced butyl rubber septum (Wheaton). One of these samples was prepared at the beginning, middle and end of the soil sample spiking process to estimate spiking solution concentration and homogeneity. It took approximately 1 hr to spike and seal the 42 soil samples, after which each one was hand shaken, mixing their contents.

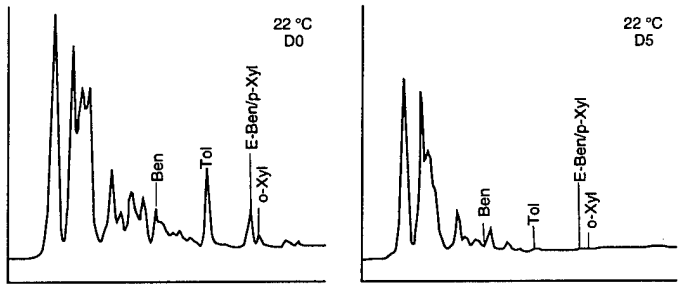
The first, middle, and last spiked soil samples, with and without $NaHSO_4$, were selected for the initial analysis. For trials 1 through 3, the initial analysis was performed on the day of treatment (day 0). However, there was a 24-hr or greater period of refrigerated equilibration between spiking and the initial analysis for trials 4 and 5. After the initial analysis, 12 sealed ampoules containing only fortified soil remained refrigerated (4°C); all of the other subsamples were held at room temperature (22°C). Triplicates from these three subsample sets (22°C preserved and unpreserved, 4°C unpreserved) were selected at random and analyzed after various storage periods up to 28 days. The samples in ampoules were prepared for analysis by placing them in auto sampler vials (22 mL) that contained 14 mL of type 1 water (MilliQ, Millipore Corp.). After sealing with a crimp-top cap, each vial was vigorously hand shaken, causing the ampoule to break and allowing the treated soil to be completely dispersed. To facilitate an HS equilibration condition, shaking continued for another two minutes after the ampoule was broken, and prior to placing in the auto sampler for analysis. Table 2 describes the holding and storage conditions for each of the five trials covered in this study.

Table 2. Sample holding and storage conditions. For each trial, 27 ampoules contained soil and 15 contained soil and 0.25 g $NaHSO_4$, prior to spiking.

Set 1,trial 1
Day 0
Spiked: 42 soil subsamples.
Stored: 12 soil samples refrigerated (4°C), 30 held at 22°C.
Analyzed: 3 VOA vials, 3 soil samples, 3 soil samples preserved with $NaHSO_4$.
Day 5, 9, 14, 21
Analyzed: 3 samples stored at 4°C, 3 samples stored at 22°C, 3 samples preserved with $NaHSO_4$.
Set 2, trial 2
Day 0 (same as set 1, trial 1)
Day 4, 8, 14, 28 (same as set 1, trial 1)
Set 3, trial 3
Day 0 (same as set 1, trial 1)
Day 3, 6, 13, 28 (same as aet 1, trial 1)
Set 1, trial 4
Day -2
Spiked: 42 soil samples
Day 0 (after two days storage at 4°C).
Stored: 12 soil samples remained refrigerated (4°C), 30 held at 22°C.
Analyzed: 3 VOA vials, 3 soil samples, 3 soil samples preserved with $NaHSO_4$.
Day 1 , 2, 3, 5
Analyzed: 3 samples stored at 22°C
Day 5, 13, 21, 28
Analyzed: 3 samples stored at 4°C, 3 samples preserved with $NaHSO_4$.
Set 4, trial 5
Day -1
Spiked: 42 soil samples
Day 0 (after one day storage at 4°C). (same as set 1, trial 4)
Day 5, 10, 14, 28 (same as set 1, trial 1)

ANALYSIS

All samples were analyzed with a headspace auto sampler (Tekmar 7000), coupled to a GC (SRI, model 8610-0058) equipped with a 15-m DB1 0.53 capillary column. The auto sampler parameters were 1) platen temperature 25°C and equilibration time 20 min., 2) loop size 1 mL, 3) loop and line temperature 100°C, 4) pressurization time 0.20 min., 5) pressurization equilibration time 0.10 min., 6) loop fill time 0.25 min., 7) loop equilibration time 0.10 min., 8) inject time 1.0 min. and 9) vial pressurization 7.5 psi. The HS sample was transferred to the GC for separation and flame ionization detection (FID). For the first two sets of analytes (set 1 and 2), the GC temperature sequence started with the injection, stayed at 40°C for 1 min., then increased to 100°C in 6 min., and was



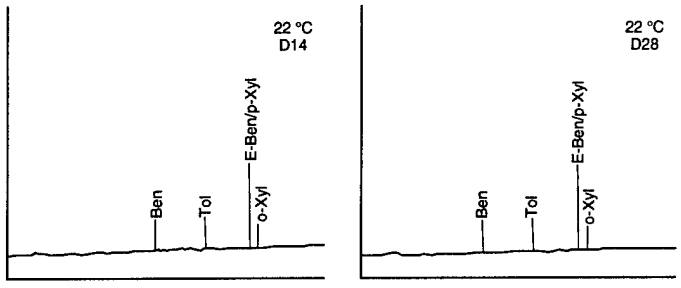
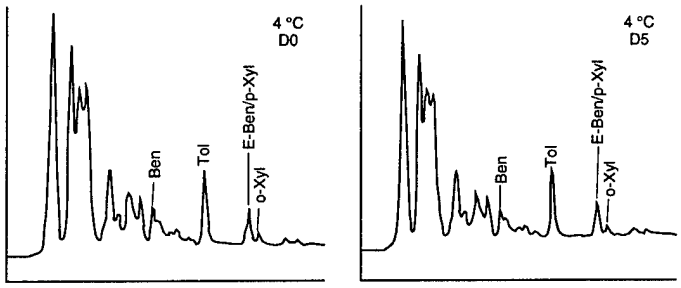


Figure 1. Gasoline-contaminated soil stored at 22 °C.



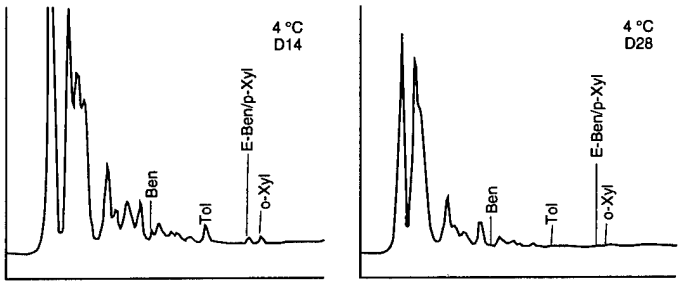
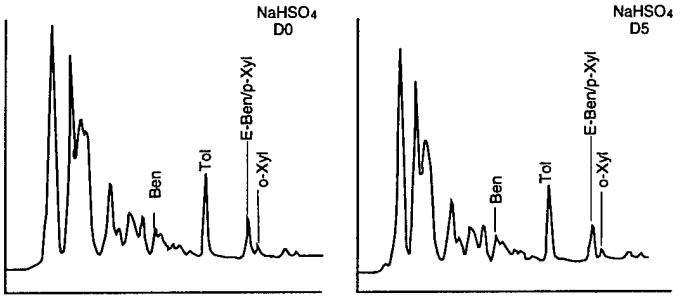


Figure 2. Gasoline-contaminated soil stored at 4 °C.



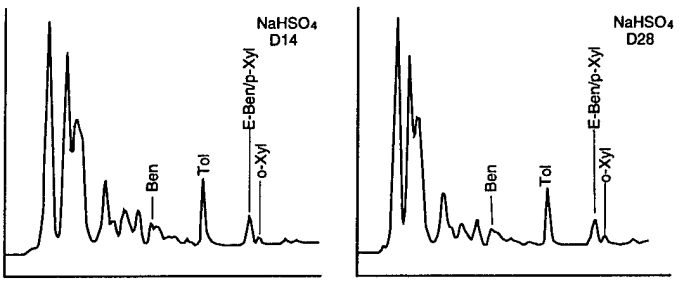


Figure 3. Gasoline-contaminated soil preserved with $NaHSO_4$ and stored at 22 °C.

held at 100°C for an additional 3.5 min. The third set of analytes used a GC program consisting of holding at 40°C for 1 min., then increasing to 150°C in 6.1 min., and holding at 150°C for an additional 3.39 min. For gasoline the following GC program was used: holding at 40°C for 1 min., and then increasing to 220°C in 8 min. Using these parameters we resolved all of the analytes in the sets 1 through 3 with the exception of E-Ben and p-Xyl (set 1). Examples of HS chromatogram for the gasoline treated soil sample (set 4) are shown in Figures 1 through 3. These chromatograms show that several aromatic compounds in gasoline could be readily identified.

Analyte concentrations were established relative to aqueous headspace standards prepared by adding small (<10 µL) quantities of a methanol (MeOH) stock solution to auto sampler vials containing 15 mL of type 1 water (Hewitt et al. 1992). For the analytes in sets 1 through 3 individual integrated peak areas or peak heights were used, while the entire chromatogram was integrated for gasoline (set 4).

RESULTS AND DISCUSSION

The concentration estimates of the individual analytes or of gasoline in the spiking solution, and in the preserved and unpreserved soil samples throughout the 28-day holding period, appear in Tables 3 through 7. The relative standard deviations (RSD) of the analyte concentrations obtained for the three aqueous aliquots representing the spiking solution, and those of the soil samples analyzed on day 0 ranged from less than 1% to 30%. The worst case was for n-butyl benzene (n-BB), which has a solubility of only 11.8 mg/L, and correspondingly resulted in the lowest treatment concentration. With the exception of this compound, the RSDs were less than 14% and averaged less than 5%, thus demonstrating that the treatment procedure was precise.

Inspection of the initial concentrations for both the unpreserved and preserved soil samples shows that they often varied from the spiking solution. The range in percentage relative differences extended from less than 1% to 68%, with concentrations both greater and less than that of the spiking solution (Tables 3–7). The worst case was for styrene in the preserved soil samples. The dramatic loss of this compound was unique to only those samples that had been treated with $NaHSO_4$. This issue will be addressed later. Of almost equal magnitude, n-BB was some 65% lower than expected. This compound, which had the poorest solubility, also has the greatest octanol–water partition (o/w) coefficient (Table 1). Correspondingly, the other analytes with large o/w coefficients also showed poor spike concentration recovery from the soil samples.

One apparent trend when using this treatment process and analysis by HS/GC is that, as the o/w partition coefficients increase, so does the discrepancy between the spiking solution and initial soil sample concentrations. An additional observation relative to the spiking solution concentrations was

Table 3. Set 1, trial 1. Mean and standard deviations of triplicate analyte concentrations of spiking solution (µg) and of analyte concentrations (µg/g) for preserved and unpreserved samples stored at 22° and 4°C.

Analyte	*Treatment aliquot (µg)*	*Analyte*	*Treatment aliquot (µg)*
TDCE	10±0.3	PCE	9.6±0.3
Ben	7.0±0.3	E-Ben	7.8±0.1
TCE	13±0.3	p-Xyl	8.2±0.1
Tol	8.5±0.2	o-Xyl	8.2±0.1

Analyte	*Storage period* Day 0†	Day 5	Day 9	Day 14	Day 21
	A. 22°C—unpreserved (µg/g)				
TDCE	9.5±0.3	9.7±0	9.3±0.1	8.7±0.1	9.3±0.3
Ben	6.6±0.1	ND*	ND	ND	ND
TCE	12±0.3	11±0.2	11±0.6	9.6±0.1	10±0.2
Tol	8.0±0.0	ND	ND	ND	ND
PCE	8.2±0.2	7.2±0.4	6.9±0.6	6.3±0.1	6.8±0.1
E-Ben	7.0±0.3	ND	ND	ND	ND
p-Xyl	7.1±0.3	0.15±0.03	ND	ND	ND
o-Xyl	7.3±0.6	5.5±0.3	ND	ND	ND
	B. 4°C—unpreserved (µg/g)				
TDCE	9.5±0.3	9.4±0.3	9.6±0.2	10±0.4	9.4±0.4
Ben	6.6±0.1	6.5±0.2	5.7±0.9	1.2±1.4	ND
TCE	12±0.3	12±0.2	12±0. 1	12±0.4	11±0.4
Tol	8.0±0.0	7.6±0.1	7.6±0.2	7.1±0.5	4.4±0.4
PCE	8.2±0.2	7.5±0.1	7.5±0.2	8.0+0.3	7.4±0.2
E-Ben	7.0±0.3	6.4±0.1	6.3±0.1	6.1±0.2	5.7±0.2
p-Xyl	7.1±0.3	6.5±0.1	6.2±0.2	6.0±0.3	4.6±0.4
o-Xyl	7.3±0.6	6.7±0.1	6.6±0.2	6.5±0.2	6.6±0.2
	C. 22°C—preserved with $NaHSO_4$ (µg/g)				
TDCE	11±0.4	11±0.2	10±0.2	9.5±0.2	10±0.3
Ben	7.5±0.2	7.4±0.1	7.4±0.2	6.5±0.1	7.3±0.2
TCE	14±0.4	13±0.4	13±1.0	11±0. 1	13±0.6
Tol	9.1±0.2	8.6±0.3	8.6±0.3	7.4±0.1	8.5±0.3
PCE	8.7±0.5	8.0±0.3	7.8±0.2	7.3±0.1	7.6±0.4
E-Ben	7.7±0.4	6.9±0.3	6.9±0.2	5.9±0.2	6.7±0.2
p-Xyl	7.7±0.2	7.0±0.2	6.9±0.2	6.1±0.2	6.6±0.5
o-Xyl	7.9±0.2	7.1±0.4	7.2±0.3	6.2±0.2	6.9±0.4

* ND = not detected, less than 0.02 µg of VOC/g.

† Same set used for day 0 values for unpreserved samples.

Table 4. Set 2, trial 2. Mean and standard deviations of triplicate analyte concentrations of spiking solution (µg) and of analyte concentrations (µg/g) for preserved and unpreserved samples stored at 22° and 4°C.

Analyte	Treatment aliquot (µg)	Analyte	Treatment aliquot (µg)
MC	11±0.3	BDCM	16±0.5
1,1 DCA	12±0.4	1,1,2 TCA	16±0.5
CF	12±0.4	CB	9.9±0.4
1,2 DCA	13±0.5	m-Xyl	12±0.6

Analyte	Storage period: Day 0†	Day 4	Day 8	Day 14	Day 28
	A. 22°C—unpreserved (µg/g)				
MC	12±0.5	11±0.3	11±0.4	10±0.2	11±0.4
1,1 DCA	12±0.3	12±0.3	12±0.4	11±0.2	12±0.4
CF	12±0.4	12±0.4	12±0.4	11±0.2	11±0.3
1,2 DCA	13±0.5	12±0.4	12±0.2	10±0.2	10±0.1
BDCM	16±0.3	15±1.0	14±0.0	14±0.3	14±0.2
1,1,2TCA	16±0.2	14±0.5	13±0.6	13±0.5	14±0.3
CB	8.7±0.3	8.3±0.3	7.8±0.3	7.5±0.2	7.4±0.1
m-Xyl	10±0.5	ND	ND	ND	ND
	B. 4°C—unpreserved (µg/g)				
MC	12±0.5	11±0.2	11±0.2	11±0.5	11±0.2
1,1 DCA	12±0.3	12±0.4	12±0.3	11±0.5	12±0.1
CF	12±0.4	12±0.2	12±0.1	11±0.5	11±0.1
1,2 DCA	13±0.5	12±0.3	12±0.2	12±0.4	12±0.2
BDCM	16±0.3	14±0.3	15±0.4	14±0.9	12±0.2
1,1,2 TCA	16±0.2	14±0.5	14±0.4	14±0.4	14±0.4
CB	8.7±0.3	8.1±0.2	8.0±0.2	7.6±0.2	8.2±0.1
m-Xyl	10±0.5	9.3±0.3	9.1±0.2	0.40±0.50	ND
	C. 22°C—preserved with $NaHSO_4$ (µg/g)				
MC	12±0.4	12±0.2	12±0.4	13±0.1	13±0.1
1,1 DCA	14±0.6	13±0.3	13±0.4	12±0.1	13±0.1
CF	13±0.5	13±0.2	13±0.3	12±0.2	13±0.2
1,2 DCA	14±0.3	14±0.1	14±0.4	13±0.3	13±0.1
BDCM	17±0.2	17±0.4	17±0.9	16±0.5	17±0.5
1,1,2 TCA	16±0.5	16±0.2	15±0.3	15±0.6	16±0.8
CB	9.4±0.4	8.4±0.1	8.1±0.3	7.5±0.2	7.7±0.1
m-Xyl	11±0.4	9.9±0.3	9.3±04	8.7±0.3	9.3±0.2

* ND = not detected, less than 0.02 µg of VOC/g.
† Same set used for day 0 values for unpreserved samples.

that the analytes with o/w partition coefficients of less than 2.6 had concentrations in the preserved soil samples that were consistently greater than the spiking solution. These two findings are consistent with analyte–organic carbon partition phenomena (Chiou 1989) and salting out (Ioffe and Vitenberg 1982). Briefly, the greater the octanol–water partition (o/w) coefficient the greater the tendency for an organic compound to partition with the organic matter present in a given soil, while salting out affects the solubility of a VOC. Since the differences in concentrations between the spiking solution and that of the preserved samples were products of both organic matter partitioning and salting out, these changes could not be compensated simply by matching the solution matrix between samples and standards (i.e., using matrix modifiers). Despite these trends, the sample treatment precision and the levels established for the analytes in the soil samples were adequate for assessing VOC concentration stability.

Consistent with previous studies where samples were held in either sealed glass ampoules or capped VOA vials (Hewitt 1994, Hewitt 1995a,b), only small decreases were observed (<35%) for the chlorinated compound concentrations. This trend was fairly independent of storage condition or preservation, and was believed to be caused by slow soil sorption (Chiou 1989). To support this

Table 5. Set 3, trial 3. Mean and standard deviations of triplicate analyte concentrations of spiking solution (μg) and of analyte concentrations (μg/g) for preserved and unpreserved samples stored at 22° and 4°C.

Analyte	Treatment aliquot (μg)	Analyte	Treatment aliquot (μg)
CDCE	12±0.7	iso-PB	3.4±0.2
C-tet	8.9±0.1	n-PB	2.8±0.2
1,2 DCP	13±0.3	1,3 DCB	4.4±0.1
Styrene	7.4±1.0	n-BB	0.81±0.21

Analyte	Storage period: Day 0†	Day 3	Day 6	Day 13	Day 28
	A. 22°C—unpreserved (μg/g)				
CDCE	11±0.4	11±0.6	9.7±0.7	7.7±1.0	7.2±0.3
C-tet	8.2±0.4	7.9±0.5	7.3±0.7	6.8±1.0	6.1±1.5
1,2 DCP	12±0.4	12±0.6	12±0.3	9.1±0.6	10±0.5
Styrene	5.9±0.2	ND	ND	ND	ND
iso-PB	2.4±0.2	0.07±0.07	ND	ND	ND
n-PB	1.7±0.2	0.04±0.03	ND	ND	ND
1,3 DCB	2.7±0.1	2.1±0.2	2.1±0.1	1.6±0.1	1.9±0.1
n-BB	0.30±0.09	0.03±0.02	ND	ND	ND
	B. 4°C—unpreserved (μg/g)				
CDCE	11±0.4	11±0.2	11±0.5	11±0.3	11±0.2
C-tet	8.2±0.4	7.8±0.5	8.0±0.1	8.0±0.2	7.8±0.6
1,2 DCP	12±0.4	12±0.2	12±0..2	12±0.4	13±0.3
Styrene	5.9±0.2	5.3±0.1	5.5±0.1	4.6±0.1	ND
iso-PB	2.4±0.2	2.1±0.1	2.1±0.1	1.9±0.1	ND
n-PB	1.7±0.2	1.4±0.1	1.5±0.1	1.2±0.1	ND
1,3 DCB	2.7±0.1	2.3±0.1	2.4±0.1	2.3±0.1	2.4±0.1
n-BB	0.30±0.09	0.21±0.01	0.23±0.01	0.16±0.01	0.02±0.02
	C. 22°C—preserved with $NaHSO_4$ (μg/g)				
CDCE	13±0.4	13±0.6	12±0.5	12±0.4	12±0.2
C-tet	8.8±0.2	8.5±0.3	8.4±0.3	8.4±0.6	8.5±0.2
1,2 DCP	14±0.1	14±0.6	14±0.3	13±0.2	14±0.6
Styrene	2.4±0.8	0.50±0.12	0.57±0.10	0.33±0.12	0.12±0.12
iso-PB	2.5±0.1	2.2±0.3	2.3±0.1	2.2±0.1	2.1±0.1
n-PB	1.8±0.1	1.5±0.2	1.6±0.1	1.5±0.1	1.4±0.1
1,3 DCB	2.6±0.1	2.2±0.3	2.2±0.1	2.1±0.1	2.0±0.1
n-BB	0.28±0.04	0.22±0.03	0.22±0.01	0.23±0.01	0.20±0.01

* ND = not detected, less than 0.02 μg of VOC/g
† Same set used for day 0 values for unpreserved samples.

theory, a second experiment with the set 1 analytes was performed, but a two-day period of refrigerated (4°C) storage was allowed between treatment and the initial analysis. This additional holding period allowed the analytes to equilibrate (sorb) with the organic carbon present in the soil. Comparing Tables 3 and 6 (Fig. 4–6 vs. 7–9) shows that while there is often a decreasing trend of the trichloroethylene (TCE) and perchloroethylene (PCE) concentrations in trial 1, this did not occur in trial 4. Based on this finding, the decreases in analyte concentrations for the chlorinated compounds in trials 1 through 3 can be partly attributed to slow sorption by the organic matter in soil.

This process is not readily reversed by aqueous extraction in preparation for static HS/GC analysis. Losses of similar magnitude (<35%) may also have occurred for the aromatic hydrocarbons in these first three trials.

All of the soil samples prepared in this study had a moisture content of 24% after treatment and were exposed to approximately 2.5 cm^3 of air during storage in the 2-mL glass ampoules. This moisture and oxygen content is sufficient to allow for the aerobic microbial degradation of the VOCs (Atlas 1981). Correspondingly, the soil subsamples held at room temperature (22°C), showed a complete (>95%) loss of the aromatic hydrocarbons within nine days (Fig. 4, 10 and 11). Indeed, among the analytes in the first three sets, with the excep-

Table 6. Set 1, trial 4. Mean and standard deviations of triplicate analyte concentrations of spiking solution (µg) after 2 and 30 days of refrigerated storage, and for analyte concentrations (µg/g) in preserved and unpreserved samples stored at 22° and 4°C.

	Treatment aliquot			*Treatment aliquot*	
Analyte	*Day 2 (µg)*	*Day 30 (µg)*	*Analyte*	*Day 2 (µg)*	*Day 30 (µg)*
TDCE	5.4±0.1	5.1±0.2	PCE	9.0±0.2	7.9±0.2
Ben	11±0.2	11±0.3	E-Ben	9.9±0.3	9.0±0.2
TCE	12±0.2	11±0.2	p-Xyl	9.2±0.1	8.6±0.2
Tol	10±0.2	9.7±0.2	o-Xyl	10±0.1	9.7±0.3

	Storage period				
Analyte	*Day 0*†	*Day 1*	*Day 2*	*Day 3*	*Day 5*
	A. 22°C —unpreserved (µg/g)				
TDCE	5.1±0.1	5.2±0.3	4.8±0.2	5.0±0.2	4.8±0.1
Ben	11±0.3	11±0.6	9.4±0.5	0.84±0.70	ND*
TCE	11±0.2	12±0.6	11±0.4	11±0.2	11±0.1
Tol	9.2±0.2	9.4±0.3	8.4±0.3	6.9±0.3	ND
PCE	7.0±0.3	7.4±0.4	6.6±0.3	7.2±0.2	7.1±0.2
E-Ben	7.7±0.4	7.8±0.4	6.7±0.2	4.4±0.3	ND
p-Xyl	7.1±0.2	7.2±0.2	6.2±0.3	6.0±0.3	0.32±0.28
o-Xyl	7.9±0.4	8.0±0.3	7.1±0.3	7.8±0.1	6.3±0.2

	Storage period				
Analyte	*Day 0*	*Day 5*	*Day 13*	*Day 21*	*Day 28*
	B. 4°C—unpreserved (µg/g)				
TDCE	5.1±0.1	4.8±0.1	4.8±0.2	4.8±0.2	4.8±0.2
Ben	11±0.3	11±0.1	4.2±0.2	ND	ND
TCE	11±0.2	11±0.1	11±0.3	11±0.2	11±0.5
Tol	9.2±0.2	8.8±0.1	8.5±0.3	5.9±0.1	1.8±0.9
PCE	7.0±0.3	7.3±0.1	7.0±0.3	7.4±0.2	7.1±0.5
E-Ben	7.7±0.4	7.7±0.2	7.4±0.3	7.3±0.1	6.7±0.4
p-Xyl	7.1±0.2	7.3±0.1	7.0±0.4	6.1±0.1	1.8±0.8
o-Xyl	7.9±0.4	8.1±0.2	7.8±0.5	7.9±0.3	7.6±0.5
	C. 22°C—preserved with $NaHSO_4$ (µg/g)				
TDCE	5.8±0.1	5.3±0.1	5.4±0.1	5.3±0.1	5.3±0.1
Ben	12±0.2	12±0.2	12±0.4	12±0.3	12±0.2
TCE	12±0.1	12±0.2	12±0.3	12±0.2	12±0.2
Tol	10±0.2	9.7±0.1	9.7±0.3	9.5±0.3	9.4±0.1
PCE	7.7±0.2	7.6±0.2	7.3±0.2	7.2±0.3	7.2±0.2
E-Ben	8.6±0.3	8.5±0.2	8.0±0.2	7.8±0.4	7.9±0.2
p-Xyl	8.0±0.1	7.7±0.1	7.6±0.2	7.2±0.3	7.2±0.1
o-Xyl	8.7±0.2	8.6±0.2	8.1±0.2	7.8±0.4	7.8±0.2

* ND = not detected, less than 0.02 µg of VOC/g

† Same set used for day 0 values for unpreserved samples

tion of ortho-xylene (o-Xyl), all of the aerobically degradable compounds were completely lost within five days (Fig. 7). The slower rate of degradation for o-Xyl is believed to be due to a steric hindrance unique to orthoisomers.* In addition, the aromatic compounds (benzene [Ben], toluene [Tol], ethyl benzene [E-Ben], para-xylene [p-Xyl] and o-Xyl) that could be easily identified in the unpreserved soil samples treated with gasoline were also lost within this 5- to 9-day period, when held at room temperature (Fig. 1). Furthermore, even the straight and branched chained aliphatics in gasoline that were not specifically identified, e.g., hexanes and pentanes, were degraded rapidly at room temperature. Overall, these rates of degradation for all of the analytes tested were consistent with those extrapolated from aqueous systems, where half-lives are on the order of days for aromatic hydrocarbons and weeks to months for the chlorinated compounds (Printup 1991).

* Personal communication with Thomas F. Jenkins, CRREL, 1995.

Table 7. Set 4, trial 5. Mean and standard deviations of triplicate gasoline concentrations of spiking solution (µg) after 1 day of refrigerated storage, and for gasoline concentrations (µg/g) in preserved and unpreserved samples stored at 22° and 4°C.

	Analyte	*Treatment aliquot (µg)*			
	gasoline	12±0.1			
	Storage period				
Analyte	*Day 0*†	*Day 5*	*Day 10*	*Day 14*	*Day 28*
	A. 22°C —unpreserved (µg/g)				
Gasoline	11±0.7	6.7±0.5	0.6±0.1	0.09±0.01	ND
	B. 4°C—unpreserved (µg/g)				
Gasoline	11±0.7	11±0.4	8.9±0.5	9.5±1.7	7.8±0.9
	C. 22°C—preserved with $NaHSO_4$ (µg/g)				
Gasoline	10±0.5	10±0.3	8.8±0.2	10±0.1	9.8±0.4

* ND = not detected, less than 0.02 µg of VOC/g

† Same set used for day 0 values for unpreserved samples

Refrigeration (4°C) slowed the rate of degradation losses, but both Ben and meta-xylene (m-Xyl) showed substantial reductions (>80%) within a 14-day storage period (Fig. 5, 8 and 12). With the exception of o-Xyl, all of the other aromatic hydrocarbons were also substantially reduced (>95%) in concentration over a 28-day period (Fig. 8, 12 and 13). These findings and others (Hewitt 1994, Hewitt 1995a,b, Turriff 1995), suggest that refrigeration is not a sufficient means of eliminating microbial degradation effects on VOC analyte concentrations in soil samples awaiting analysis.

In contrast, with the exception of styrene, all of the aromatic analytes tested and the majority of compounds present in gasoline were preserved with $NaHSO_4$ (Fig. 3, 6, 9, 14 and 15). The small (<30%) concentration reductions that were observed relative to day 0 can be partly attributed to slow sorption by the soil organic matter and lack of an equilibration period between treatment and the initial analysis. Additional evidence for this mechanism is shown by the greater losses for compounds with the largest o/w partition coefficients (n-propyl benzene [n-PB], iso-propyl benzene [iso-PB], 1,3 dichlorobenzene [1,3 DCB], and n-BB), and by the trend showing that the greatest reductions in concentrations almost always occurred between the first two analyses (day 0 to day 3 to 5, trials 1 through 3). Since a equilibrium condition most likely has already been reached for environmental samples, VOC losses of this nature would not be anticipated for samples taken during a site investigation and preserved with $NaHSO_4$.

Styrene was not stable in the soil preserved with $NaHSO_4$, perhaps because it either rapidly polymerized or was chemically transformed into an alcohol.* Since there was not enough water present to create a slurry condition, $NaHSO_4$ may be either present as a salt or an acid. An additional experiment not reported here showed that the loss of styrene was unique to soil samples preserved with $NaHSO_4$; i.e., no losses were seen in laboratory water that was similarly preserved and stored. Thus, the chemical reaction that transforms styrene most likely is catalyzed by the soil. Clearly, soil sample preservation by $NaHSO_4$, or perhaps any acid, would not be compatible for investigations where styrene is a constituent of interest.

Although these experiments used only laboratory-fortified samples, field samples should behave similarly because chemical preservatives inhibited the activity of the indigenous soil microbes. There are, however, some issues that need to be addressed aside from the chemical transformation of styrene in soil due to preservation with $NaHSO_4$:

1. How should the samples be collected?
2. Are there any effects due to storage of samples in VOA vials?
3. Do all soil samples require chemical preservation?
4. Is it important to obtain a pH of 2 or lower throughout the sample to inhibit microbiological degradation?

While losses of greater than 80% for some analytes may be attributed to biodegradation when soil samples held refrigerated for 14 days, much

* Personal communication with Thomas F. Jenkins, CRREL, 1995.

greater losses occur when sample collection and handling operations do not maintain the structural integrity or limit atmospheric exposure (Hewitt et al. 1995). For instance, bulk samples that are transferred to glass bottles using spatulas, spoons, or paint scrapers, from which subsamples will be removed for analysis after several days of storage, are often reduced in VOC concentration by between 90 and 99.9% as compared to samples collected using a single nondisruptive transfer method (Hewitt 1994, Hewitt et al. 1995). Clearly, how the sample is collected and handled has a

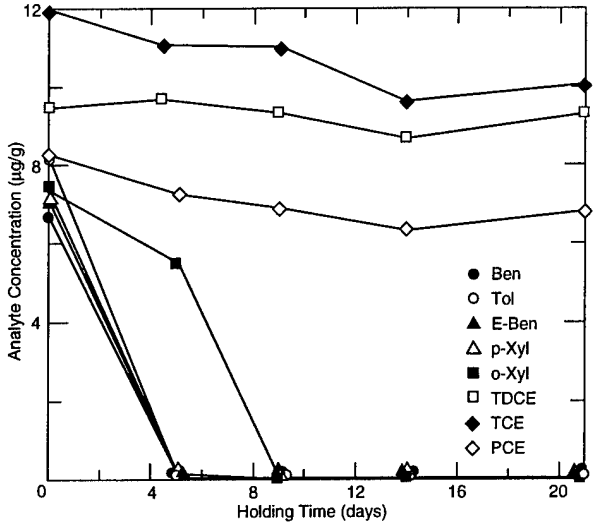


Figure 4. Set 1/trial 1. Contaminated soil stored at 22°C.

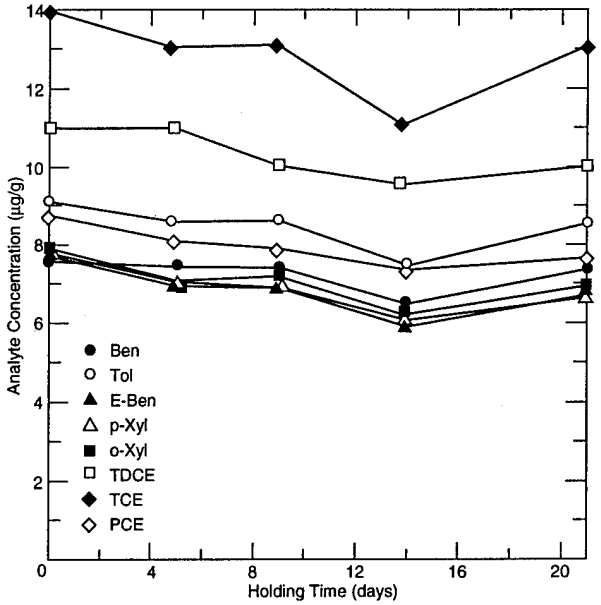


Figure 6. Set 1/trial 1. Contaminated soil preserved with $NaHSO_4$ and stored at 22°C.

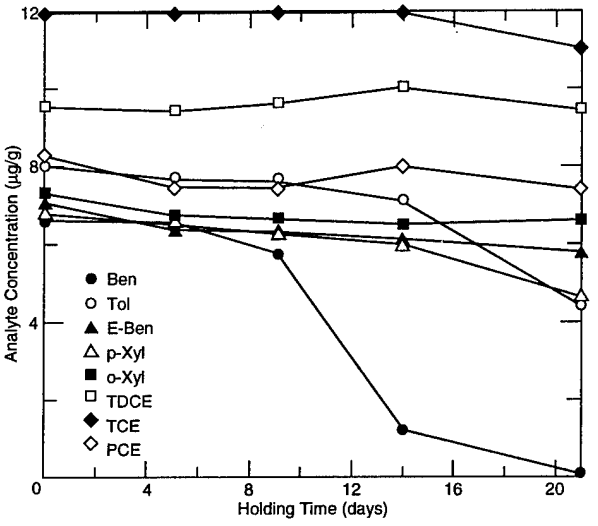


Figure 5. Set 1/trial 1. Contaminated soil stored at 4°C.

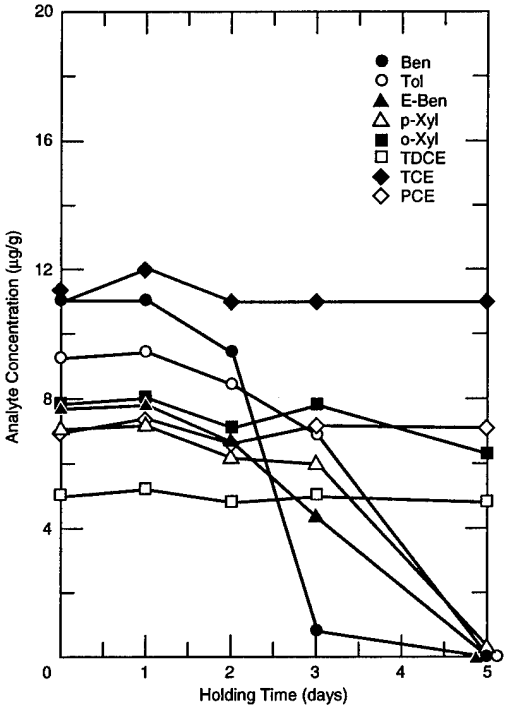


Figure 7. Set 1/trial 4. Contaminated soil stored at 22°C.

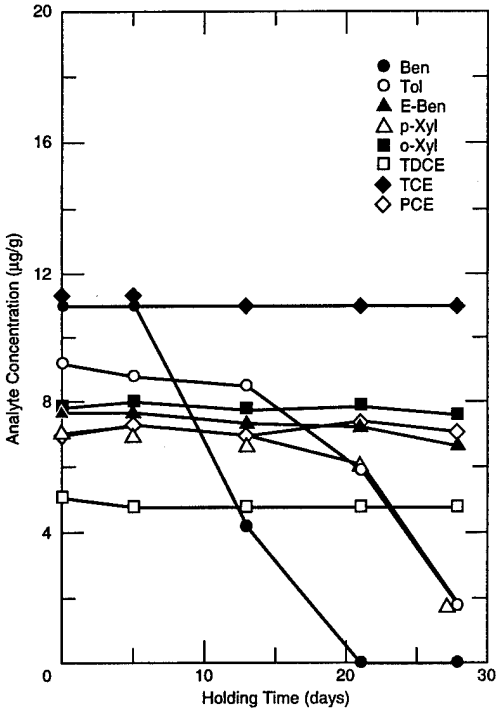


Figure 8. Set 1/trial 4. Contaminated soil stored at 4°C.

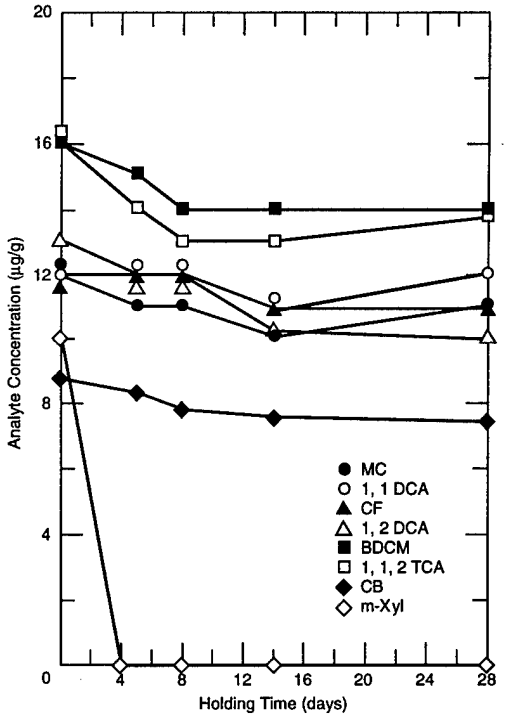


Figure 10. Set 2/trial 2. Contaminated soil stored at 22°C.

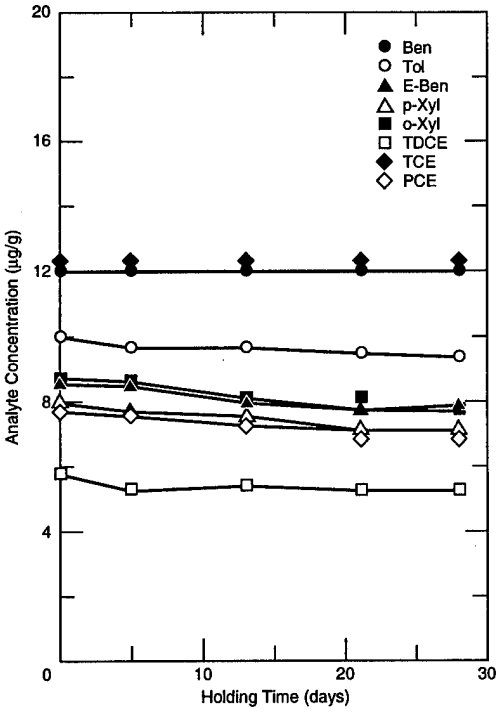


Figure 9. Set 1/trial 4. Contaminated soil preserved with $NaHSO_4$ and stored at 22°C.

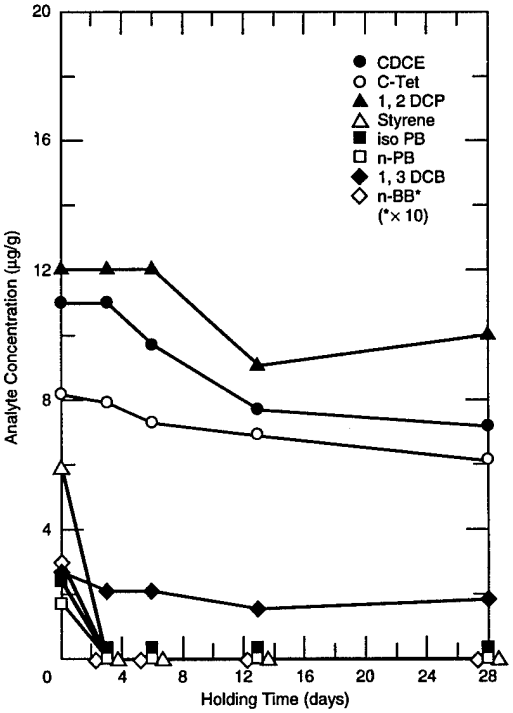


Figure 11. Set 3/trial 3. Contaminated soil stored at 22°C.

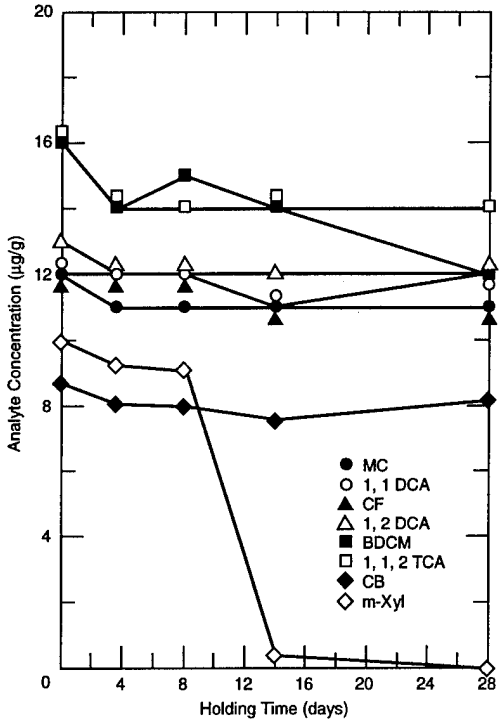


Figure 12. Set 2/trial 2. Contaminated soil stored at 4°C.

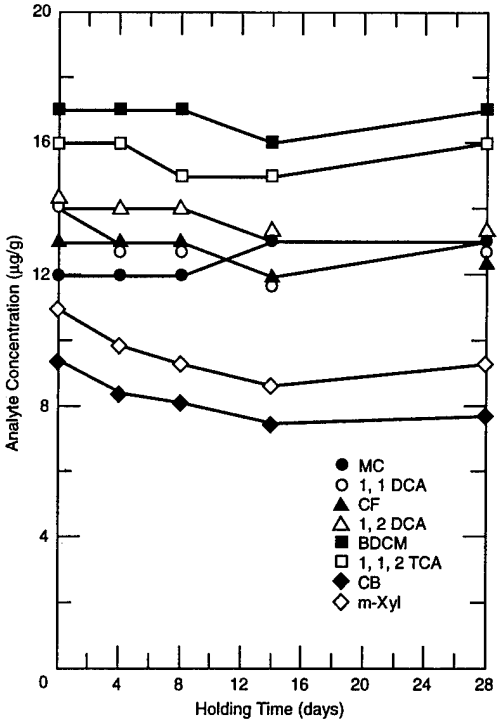


Figure 14. Set 2/trial 2. Contaminated soil preserved with $NaHSO_4$ and stored at 22°C.

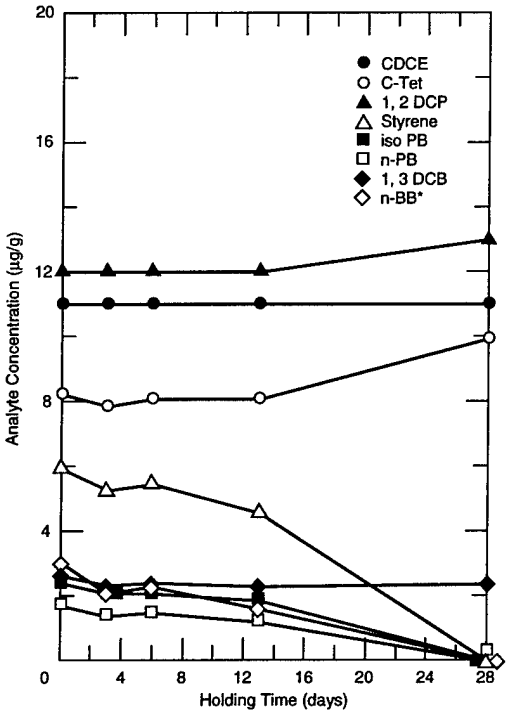


Figure 13. Set 3/trial 3. Contaminated soil stored at 4°C.

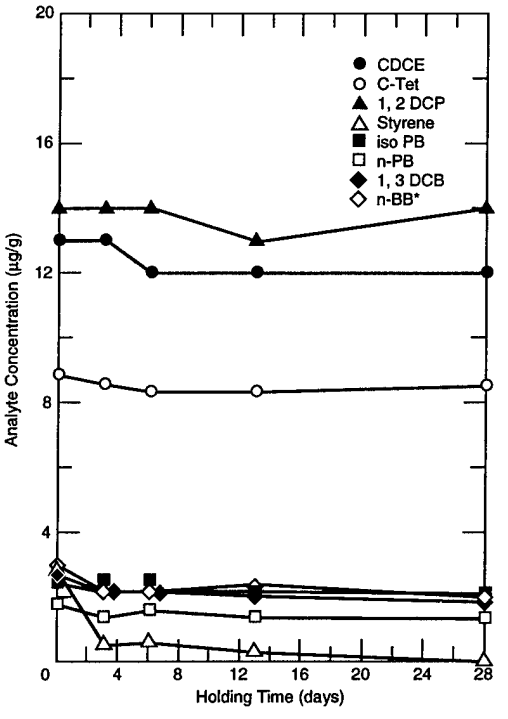


Figure 15. Set 3/trial 3. Contaminated soil preserved with $NaHSO_4$ and stored at 22°C.

much bigger effect on the concentration of the VOCs than biological degradation. However, if measures are taken to limit exposure and maintain the structure of the soil during collection, and if the soil sample is transferred to a vapor-tight bottle from which it can later be analyzed, then additional precautions to prevent biological degradation should be taken.

All the samples in this study were stored in sealed glass ampoules, vessels that do not lend itself to field sampling practices, and to which samples could not be transferred without significant volatilization losses. One of the more common vessels for soil sample collection, storage and shipping is VOA vials. These vials have a Teflon-faced silicone septum for the purpose of sealing and inhibiting VOC losses; however, this polymeric material has been shown to sorb VOCs from solution (Gilham and O'Hannesin 1990; Parker and Ranney 1994; Parker and Ranney, in press).

To see if VOCs associated with soils stored in a VOA vial would also tend to be lost to Teflon, the following experiment was performed. Eighteen aqueous samples of the set 1 analytes were prepared by spiking 30 mL of laboratory water preserved with 0.25 g of $NaHSO_4$ and stored refrigerated (4°C) in 40-mL VOA vials (Eagle Picher). Half of these replicate solutions were stored upright and half were stored inverted. Triplicate samples of each type were removed and analyzed after 7, 14 and 21 days of storage, and analyte concentrations were determined based on a fresh standard prepared from the same stock solution used to prepare the samples. In this case all analyses were performed on a field-portable Photo-Vac 10S10 gas chromatograph (Hewitt et al. 1992).

The results of this experiment showed that PCE in either the gaseous or liquid phase tended to be lost from the vials (Table 8, Fig. 16). Similar results were established for unpreserved aliquots of the spiking solution transferred to 20-mL auto sampler VOA vials with Teflon-lined caps (Wheaton, Table 6). Perchloroethylene had been identified as one of the analytes showing the greatest rate of loss in earlier solution studies (Parker and Ranney 1994, Parker and Ranney in press). Based on these findings we can assume that some small losses (5 to 15%) will be incurred when either a soil or liquid sample contaminated with VOCs is stored for an extended period (28 days) in a VOA vial with a Teflon-lined cap. However, the probable loss mechanism results from the ability of VOCs to pass through this material and not because of sorption (Barbeau et al. 1995). Sorption

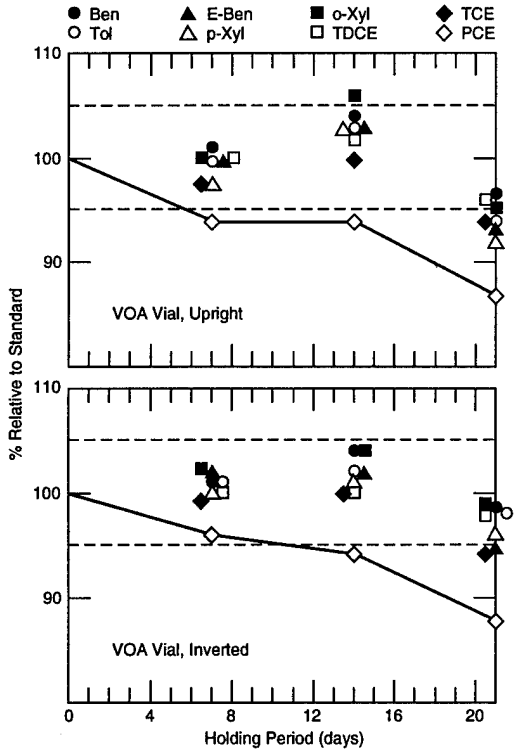


Figure 16. Aqueous solution of set 1 analytes preserved with $NaHSO_4$ and stored at 4°C.

Table 8. Response (× 100) relative to fresh standard of solutions preserved with $NaHSO_4$ and held refrigerated in either an upright or inverted position.

	Storage period		
Analyte	*Day 7*	*Day 14*	*Day 21*
	Upright		
TDCE	99.1±1.0*	102±4.9	96.2±3.6
Ben	101±0.1	104±5.3	96.5±0.0
TCE	97.7±0.7	100±4.6	94.1 ±5.2
Tol	99.7±1.1	103±4.8	95.2±1.7
PCE	94.3±0.6	93.9±4.6	86.9±6.1
E-Ben	99.4±12	103±7.12	93.4±3.2
p-Xyl	97.7±1.7	103±2.3	92.0±5.5
o-Xyl	100±0.4	106±1.7	95.3±2.4
	Inverted		
TDCE	99.7±1.1	100±0.8	97.7±2.7
Ben	101±1.4	104±2.1	98.6±2.0
TCE	99.3±0.7	100±2.1	94.4±2.4
Tol	101±1.0	102±2.2	97.9±0.9
PCE	95.9±0.7	94.2±1.4	87.7±3.6
E-Ben	102±0.8	102±3.1	94.8±3.1
p-Xyl	99.9±0.7	101±3.2	96.3±1.4
o-Xyl	102±1.6	104±5.8	98.7±2.7

Average and standard deviations $n = 3$.

onto glass is another possible explanation, but appears unlikely in light of the stability of this analyte in glass ampoules for the experiment with an equilibration period (Table 6).

Furthermore, these losses are analyte specific and are likely to be condition dependent (i.e., storage temperature); thus more detailed studies are warranted. Until such information is available, we recommend that even chemically preserved samples be stored refrigerated.

The soil in this study was obtained within 10 cm of the ground surface. In this horizon there is typically more organic carbon and consequently more biological activity, as compared to soils obtained from greater depths in the vadose zone. However, substantial evidence exists showing that even subsurface soils with organic carbon of less than 0.5% become biologically active once oxygenated. Hence in-situ aeration systems are being developed to enhance bioremediation of subsurface oil and gasoline spills (Downey et al. 1994, Germann and Friesen 1994). Since all conventional sampling methods expose soil samples to the atmosphere during collection and handling operations, previously oxygen limited biodegradation reactions could be initiated. For this reason chemical preservation is likely to be necessary whenever aromatic hydrocarbons are of concern.

With regard to whether a slurry condition is needed to evenly distribute the preservative, an earlier experiment where 1 mL of water was added to preserved soil ampoules before spiking to slurry the soil matrix (Hewitt 1995b) was not significantly different (95% confidence level) from those without excess water. However, laboratory-treated soil does not mimic the cohesiveness of a native soil. Until more information is available, a conservative approach should be recommended. Therefore, enough water should be present in the VOA vial to create a slurry condition, once the soil sample has been introduced. Furthermore, preservation methods that would not rely on acidification (i.e., mercuric chloride) would be necessary when carbonates were present.

CONCLUSION

By preserving with $NaHSO_4$, treated soil samples held at 22°C showed stable VOC concentrations for up to 28 days. This chemical preservation method would complement collection protocols that minimize volatilization losses during collection, storage and analysis for soil with low carbonate levels. Confinement of samples in vaportight vessels throughout handling and analysis procedures is critical to the accurate assessment of both biological degradation and chemical preservation of VOCs in soil. Using such protocols allows investigators to determine if measures other than refrigeration are necessary or effective in maintaining stable VOC concentrations over regulated holding times.

LITERATURE CITED

Atlas, R.M. (1981) Microbial degradation of petroleum hydrocarbons: An environmental perspective. *Microbiological Reviews,* **45**: 180–209.

Barbeau, D.S., T.G. Ellis and C.P.L. Grady, Jr. (1995) Oxygen leakage during respirometric measurement: A caution on the use of PTFE tape. *Water Resources,* **29**(4) 1211–1212.

Chiou, C.T. (1989) *Reactions and Movement of Organic Chemical in Soils* (B.L. Sawhney and K. Brown, Eds.). Madison, Wisconsin: Soil Science Society of America, Special Publication 22, p. 1–29.

Downey, C.D., P.R. Guest and J.W. Ratz (1994) Results of a two-year in situ bioventing demonstration. In *Proceedings of the 18th Annual Army Environmental Technology Symposium, Williamsburg, Virginia, June,* p. 223–234.

Germann, G.G. and K. Friesen (1994) Pilot test for integrated in situ and ex situ bioremediation of petroleum-contaminated soil at a fuel storage facility in Virginia. In *Proceedings of the 18th Annual Army Environmental Technology Symposium, Williamsburg, Virginia, June,* p. 215–222.

Gilham, R.W. and S.F. O'Hannesin (1990) Sorption of aromatic hydrocarbons by materials used in construction of ground-water sampling wells. In *Ground Water and Vadose Zone Monitoring, ASTM STP 1053,* p. 108–122. Philadelphia, Pennsylvania: American Society for Testing and Materials.

Hewitt, A.D. (1995a) Preservation of volatile organic compounds in soil subsamples. *American Environmental Laboratory,* August.

Hewitt, A.D. (1995b) Determining volatile organic compound concentration stability in soil. In *Proceedings of 11th Annual Waste Testing and Quality Assurance Symposium, July 23–28, 1995, Washington, D.C.,* p. 173–183.

Hewitt, A.D. (1994) Concentration stability of four volatile organic compounds in soil subsamples. USA Cold Regions Research and Engineering Laboratory, Special Report 94-6.

Hewitt, A.D., T.F. Jenkins and C.L. Grant (1995)

Collection, handling, and storage: Keys to improved data quality for volatile organic compounds in soil. *American Environmental Laboratory,* January–February.

Hewitt, A.D., P.H. Miyares, D.C. Leggett and T.F. Jenkins (1992) Comparison of analytical methods for determination of volatile organic compounds. *Environmental Sciences Technology,* **26**: 1932–1938.

Ioffe, B.V., A.G. Vitenberg (1982) *Head-Space Analysis and Related Methods in Gas Chromatography.* New York: John Wiley & Sons.

Jackson, J., N. Thomey and L.F. Dietlein (1991) Degradation of hydrocarbons in soil samples analyzed within accepted analytical holding times. In *5th Outdoor Action Conference on Aquifer Restoration, Ground Water Monitoring, and Geophysical Methods, Las Vegas, Nevada, May 1316,* p. 567–576.

King, P. (1993) Evaluation of sample holding times and preservation methods for gasoline in fine-grained sand. In *National Symposium on Measuring and Interpreting VOCs in Soils: State of the Art and Research Needs, Las Vegas, Nevada, January 12–14, 1993.*

Maskarinec, M.P., C.K. Bayne, R.A. Jenkins, L.H. Johnson and S.K. Holladay (1992) Stability of volatile organics in environmental soil samples. Office of Scientific and Technical Information, Oak Ridge, Tennessee, ORNL/TM12128.

Maskarinec, M.P., L.H. Johnson, S.K. Holladay, R.L. Moody and R.A. Jenkins (1990) Stability of volatile organic compounds in environmental water samples during transport and storage. *Environmental Sciences Technology,* **24**: 1665–1670.

Parker, L.V. and T.A. Ranney (in press) Sampling trace-level organics with polymeric tubing. USA Cold Regions Research and Engineering Laboratory, Special Report.

Parker, L.V. and T.A. Ranney (1994) Effect of concentration on sorption of dissolved organics by well casings. *Ground Water Monitoring and Remediation,* **14**(3): 139–149.

Printup, H.T. (Ed.) (1991) *Handbook of Environmental Degradation Rates.* Chelsea, Michigan: Lewis Publishers, Inc.

Turriff, D. (1995) Comparison of alternatives for sampling and storage of VOCs in soil. In *Proceedings of 11th Annual Waste Testing and Quality Assurance Symposium, July 23–28, Washington D.C., 1995,* p. 51–58.

U.S. EPA (1986) *Test Methods for Evaluating Solid Waste,* Vol. 1B. U.S. Environmental Protection Agency, SW–846.

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13. ABSTRACT (*Maximum 200 words*)

Sodium bisulfate ($NaHSO_4$) was evaluated as a means of chemically preserving soil samples to prevent the microbiological degradation of volatile organic compounds (VOCs). Laboratory sample treatment consisted of spiking soil samples held in glass ampoules with aqueous solutions containing eight different VOCs or gasoline and then sealing them to eliminate volatilization as a concern. Samples preserved with $NaHSO_4$ were held at room temperature (22°C), while equal numbers of unpreserved samples were stored refrigerated (4°C) and at room temperature. Results show that concentrations of all of the halogenated hydrocarbons tested (14) remain fairly constant, independent of temperature or preservation. In contrast, all the aromatic hydrocarbons (10) tested as separate analytes, or ones that could easily be identified in gasoline, experienced a complete (>95%) loss when held for nine days at room temperature. Refrigeration reduced the rate of biodegradation, but two aromatic hydrocarbons showed substantial losses (>80%) within the currently recommended 14-day holding period. Over a 28-day refrigerated period, reductions of greater than 95% occurred for 9 of 10 aromatic hydrocarbons tested. With the exception of styrene, chemical preservation by introducing $NaHSO_4$ mitigated the loss of all of aromatic hydrocarbons tested over a 28-day holding period when samples were stored at room temperature. Therefore, $NaHSO_4$ preservation is one way of effectively eliminating biodegradation of VOCs in soil samples intended for low level (<1-μg/g) analysis.

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